PATENT
Docket No. 357972800700
Client Reference 97B058/2 (Asset #21)

CERTIFICATE OF MAILING BY "FIRST CLASS MAIL"

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on July 27, 1999.

Sherri N. Shipe

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of:

S.N. VAUGHN

Serial No.: 08/943,399

Filing Date: October 3, 1997

For: METHOD FOR INCREASING LIGHT OLEFIN YIELD BY CONVERSION OF A HEAVY HYDROCARBON FRACTION OF A PRODUCT TO LIGHT OLEFINS

Examiner: In Suk Bullock

Group Art Unit: 1764

DECLARATION UNDER 37 C.F.R. 1.131

Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

1. This declaration is to establish completion of the invention in this application in the United States, at a date prior to July 22, 1997, the effective date of U.S. Patent No. 5,914,433.

2. The person making this declaration is the inventor.

3. To establish the date of completion of the invention of this application, attached is a copy of Patent Memorandum PM97019 redacted form. PM97019 includes a complete description of the claimed invention. In addition, PM97019 includes actual data showing an actual completion or reduction to practice of the invention.

4. I have reviewed what I believe to be an exact photocopy of the original Patent Memorandum PM97019, which bears the signature of D.Y. Ou as having witnessed, read and understood the document on a date prior to July 22, 1997. D.Y. Ou is presently Engineering Associate at Exxon Chemical Company, and was employed by Exxon Chemical Company at the time of having witnessed, read and understood Patent Memorandum PM97019.

5. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: 7/22/99 By: Stephen N. Vaughn
Stephen N. Vaughn

"[redacted]7019 Exhibit A

PATENT MEMORANDUM

EXXON CHEMICAL COMPANY

INVENTOR(S): Stephen N. Vaughn	DIVISION MEMO NO / CLASS
EXACT DESCRIPTIVE TITLE: Process to convert C4+ Stream in Methanol to Olefins Process	
PATENT COMMITTEE	BRIEF ABSTRACT OF INVENTION: Hydrocarbons heavier than propane are separated from a Methanol to Olefins product stream and converted to generate additional ethylene and propylene either in a separate reactor or in the MTO reactor.
STATUS OF INVENTION (EXISTING OR CONTEMPLATED EXPERIMENTAL, COMMERCIAL OR PLANT SCALE USE): Experimental	
DATE OF FIRST USE, PUBLICATION, AND/OR SALE	
WERE YOU WORKING FULL OR PART TIME ON ANY GOVERNMENT CONTRACT AT, OR WITHIN ONE YEAR PRIOR TO THE TIME THE INVENTION WAS FIRST CONCEIVED OR TESTED? ☐ YES ☒ NO CONTRACT NO.(S)_____	FOR LAW-TECHNOLOGY DEPARTMENT USE ONLY — DATE RECEIVED [redacted] ATTORNEY'S INIT.

FIRST WRITTEN DESCRIPTION DATE [redacted]	HEREWITH OR FILED AT: Notebook No 19763 p 59	DATE OF FIRST TEST [redacted]	WHERE RECORDED? (E.G. NOTEBOOK & PAGE): Notebook 19763 p 59
FIRST SKETCH OR DRAWING DATE [redacted]	HEREWITH OR FILED AT: Herewith	COMPANY REPORTS, FILE MEMOS, PM'S RELATED TO INVENTION (IDENTIFY): none	
FIRST DISCLOSURES TO OTHERS DATE [redacted]	TO WHOM AND WHERE: TJ Chen BCIT, Baytown Tx	IS MODEL OR PROTOTYPE AVAILABLE? ☐ YES ☒ NO	

DETAILED DESCRIPTION OF INVENTION (SEE INSTRUCTIONS ON REVERSE SIDE)

The Methanol-to-Olefins (MTO) process as currently envisioned is remarkably selective to ethylene and propylene. Depending upon the process conditions used, $C_2^= + C3^=$ yields of 80-90% are expected to be achieved. Even with this highly selective process however, approximately 5-10% of the organic portion of the methanol feed ends up as relatively low value C_4^+ olefins.

To make better use of this stream, it has been discovered that the C_4^+ olefins can be recycled to produce additional ethylene and propylene. As an example of this, Table 1 illustrates that when 1-butene is reacted over an MTO catalyst, propylene, ethylene and C5+ are generated as products. It is believed that a significant fraction of the C_4^+ stream will ultimately form coke. Tests using 1-butene as a surrogate for the C_4^+ stream show a selectivity of approximately 10.1 % to coke. If the other heavy products react in the same way, the typical yield of approximately 12% C_4^+ products in unrecylcled MTO can be replaced with 1.4% $C2^=$ and 8.0% $C3^=$ and 1.5 % coke when the C_4^+ stream is recycled to extinction in the MTO reactor. Other yields will be realized if the C_4^+ stream is converted in a separate reactor as described below. The extra coke can be burned in the catalyst regenerator for heating value and the plus $C2^=$ and $C3^=$ provides additional high value products.

The recycle can be accomplished in at least two ways. As Figure 1 shows schematically, the C_4^+ products can be separated from the more valuable $C2^=$ and $C3^=$ cryogenically and the entire C_4^+ stream (or partof that stream) can be combined with the methanol feedstream. [Note:The cryogenic separation shown in Figs 1 and 2 is intended to be generic and does not preclude the inclusion of additional separation steps neccesary to produce ethylene and propylene of the required purity, while producing a stream composed substantially of C4+ products that can be further converted as described in this invention]. After reaction in the MTO reactor, the heavy stream comprising C_4^+ products produced from both methanol and previously recycled C_4^+ products can be again separated and recycled; this process can be continued until no net C_4^+ products are produced or alternatively, sized to produce a specific amout of C_4^+ products .

(Continue Description on Additional Sheets)

INVENTOR(S)

SIGNATURE (FIRST NAME IN FULL) Stan Vaughn	SIGNATURE (FIRST NAME IN FULL)
WITNESSED, READ & UNDERSTOOD BY [signature] DATE [redacted]	WITNESSED, READ & UNDERSTOOD BY DATE
INVENTOR EMPLOYMENT CONTRACT ☐ YES ☐ NO CITIZENSHIP: ☐ U.S.A. ☐ OTHER_____	INVENTOR EMPLOYMENT CONTRACT ☐ YES ☐ NO CITIZENSHIP: ☐ U.S.A. ☐ OTHER_____
EXXON CHEMICAL CO. DIVISION: BC IT OTHER:	EXXON CHEMICAL CO. DIVISION: OTHER:

PATENT MEMORANDUM

Page No. 2

(For Continued Detailed Description of Invention)

INVENTOR(S)
Stephen N. Vaughn

EXACT DESCRIPTIVE TITLE
Process to convert C4+ Stream in Methanol to Olefins Process

In this mode of operation, one additional benefit to the overall MTO process is the inclusion in the MTO reactor of a certain amount of endotheric C_4^+ cracking reactions which will help to counteract the exothermic MTO reactions.

Alternatively, as illustrated schematically in Fig 2, after cryogenic separation the C_4^+ stream can be fed into a relatively small auxiliary reactor. By using a separate reactor, process conditions and catalysts can be selected to optimize the production of the desired products. As examples of the benefits of reacting the C_4^+ stream under conditions different from optimal MTO conditions, Table 2 illustrates the effect of using ZSM-5. ZSM-5 is not generally considered to be a good MTO catalyst but it has a higher activity for butene conversion than does the SAPO-34 catalyst.

The current invention encompasses the idea of separating C_4^+ products from an MTO product stream (by means well known to those skilled in the art) and directing this separated stream to either 1) the MTO conversion reactor or 2) a separate C_4^+ conversion reactor. In the first case the conversion of C_4^+ will be achieved on the MTO conversion catalyst at conditions favorable for MTO. In the second case, a number of catalysts can be employed including SAPO-34, -44,-18, and -17, ZSM-5 or medium pore zeolites. The process conditions in the second case can be optimized independently of the MTO conversion reactor and are expected to be in the ranges of

WHSV	0.1 to 100 hr-1
Temperature	300-650 °C
Pressure	15-100 psia
Dilution	none or steam

Again depending upon the catalyst employed, on-line or periodic regeneration of the C_4^+ conversion catalyst may be provided by means well known to those skilled in the art.

In either case it may be advantageous to provide for some C_4^+ product purge --to provide a ready source of fuel gas for plant use, C_4^+ product for sale or to limit the size of the recycle stream.

25 psig /WHSV 120 hr-1/ pure 1-butene/450 °C

Table 1

		Selectivity (wt%, excluding coke and water)				
Feed	Conversion	CH4	C2=	C3=	C4	C5+
1-C4=	34.23	0.10	10.57	66.29	N/A	21.74
MeOH	100.00	0.86	51.06	34.19	9.29	2.08

25 psig /WHSV 120 hr-1/ pure 1-butene/450 °C

Table 2

		Selectivity (wt%, excluding coke and water)				
Catalyst	Conversion	CH4	C2=	C3=	C4	C5+
SAPO-34	34.23	0.10	10.57	66.29	N/A	21.74
ZSM-5	73.10	0.21	22.31	53.03	N/A	19.91

INVENTOR(S)

1		2	
SIGNATURE (FIRST NAME IN FULL)		SIGNATURE (FIRST NAME IN FULL)	
WITNESSED, READ & UNDERSTOOD BY	DATE [redacted]	WITNESSED, READ & UNDERSTOOD BY	DATE

PATENT MEMORANDUM

Page No. 3

(For Continued Detailed Description of Invention)

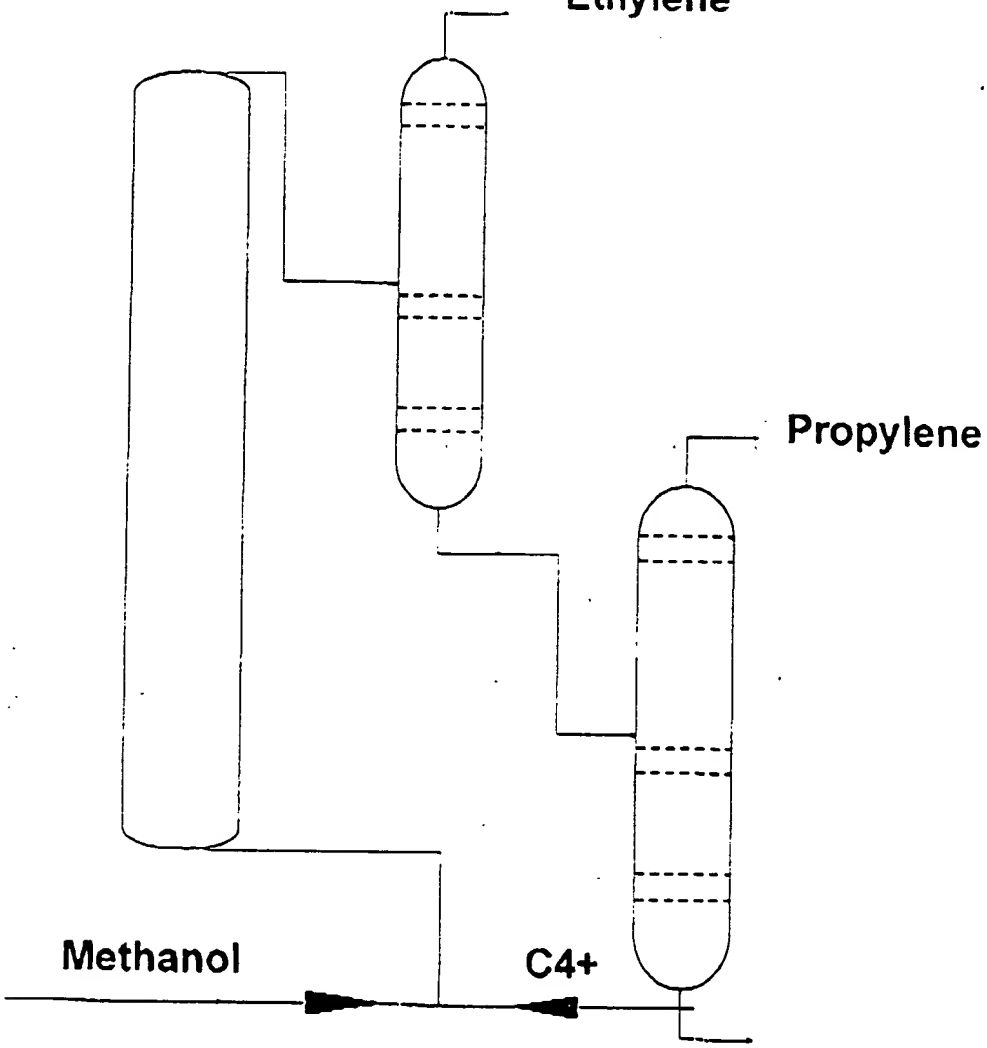
INVENTOR(S)

S. N. Vaughn

EXACT DESCRIPTIVE TITLE

Process to convert C4+ Stream in Methanol to Olefins Process

Fig 1



INVENTOR(S)

1		2	
SIGNATURE (FIRST NAME IN FULL)		SIGNATURE (FIRST NAME IN FULL)	
WITNESSED, READ & UNDERSTOOD BY	DATE [redacted]	WITNESSED, READ & UNDERSTOOD BY	DATE

PATENT MEMORANDUM

Page No. 4

(For Continued Detailed Description of Invention)

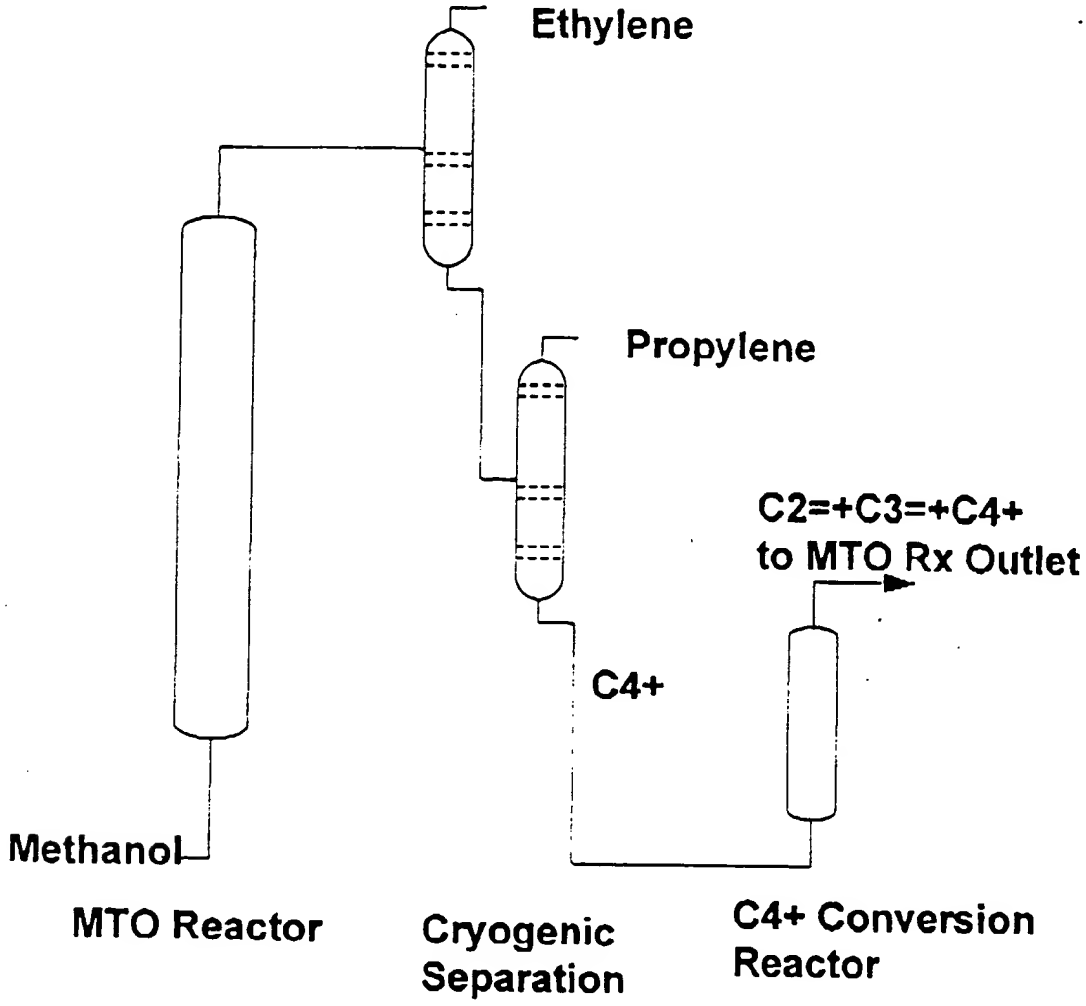
INVENTOR(S)

S. N. Vaughn

EXACT DESCRIPTIVE TITLE

Process to convert C4 + Stream in Methanol to Olefins Process

Fig 2



INVENTOR(S)

1		2	
SIGNATURE (FIRST NAME IN FULL) Steven Vaugh		SIGNATURE (FIRST NAME IN FULL)	
WITNESSED, READ & UNDERSTOOD BY	DATE [redacted]	WITNESSED, READ & UNDERSTOOD BY	DATE